공학석사 학위논문

CHARACTERIZATION OF ARSENATE AND CHROMATE REMOVAL FROM INDUSTRIAL WASTEWATER BY MODACRYLIC ANION EXCHANGE FIBERS

모드아크릴 음이온교환섬유를 이용한 산업폐수 내 5가 비소와 6가 크롬 제거 특성 연구

2017년 12월

서울대학교 대학원

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이 승 찬

Characterization of arsenate and chromate removal from industrial wastewater by modacrylic anion exchange fibers

A THESIS

SUBMITTED TO THE DEPARTMENT OF LANDSCAPE ARCHITECTURE AND RURAL SYSTEMS ENGINEERING AND THE COMMITEE ON GRADUATE STUDIES OF SEOUL NAIONAL UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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지도교수 김 성 배

이 논문을 공학석사 학위논문으로 제출함

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생태조경·지역시스템공학부 지역시스템공학전공

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ABSTRACT

This thesis aims to characterize the removal of arsenate and chromate from industrial wastewater by modacrylic anion exchange fibers. The physicochemical features of three anion exchange fibers (Kanecaron^{TM} KC31, SA, and SA2) and the factors that influence on removal of arsenate and chromate by the fibers were carefully examined.

Field emission scanning electron microscopy (FESEM) images indicate that three fibers were micron-sized and cylindrical. The result of energy dispersive X-ray spectroscopy (EDS) revealed that the fibers are composed of carbon (C), nitrogen (N), oxygen (O) and chloride (Cl). Anion exchange capacity analysis showed that the pristine KC31 has 4.70 mmol/g of functional groups (free amine form), SA has 1.15 mmol/g of functional groups (fully protonated amine), and SA2 has 2.65 mmol/g of those (1.34 mmol/g of protonated amine and free amine form the others).

From the results of pH experiments, As(V) removal by KC31 was highest at pH 4 (9.480 mg/g) and Cr(VI) at pH 2 (47.89 mg/g). As(V) removal by SA was highest at pH 10 (9.753 mg/g) and Cr(VI) at pH 4

(47.16 mg/g). In case of SA2, As(V) removal was highest at pH 10 (8.419 mg/g) and Cr(VI) at pH 6 (48.99 mg/g). The maximum removal capacity for As(V) of three fibers from Langmuir models were 47.16 mg/g (KC31), 47.19 mg/g (SA), and 38.05 mg/g (SA2). The maximum removal capacity for Cr(VI) of the fibers from Langmuir models were 250.2 mg/g for KC31, 162.5 mg/g for SA, 161.0 mg/g for SA2. At kinetic experiments, the fibers could reach equilibrium in reaction with As(V) and Cr(VI) in an hour. Arsenate or chromate adsorbed to fibers was successfully washed off with NaCl solutions, resulting in little changes of removal capacity over five adsorption-desorption cycles.

Considering high heavy metal removal ability in acidic condition and large ion exchange capacity, KC31 was chosen as the proper adsorbent for two in order to treat acidic mining wastewater and chromium-plating rinse water. Columns filled with KC31 treated 1,145 mg of As(V) (flow rate : 1.0 mL/min), 2,890 mg of Cr(VI) (flow rate : 0.5 mL/min), and 2,390 mg of Cr(VI) (flow rate : 1.0 mL/min) under flow-through conditions.

This study indicates that the anion exchange fibers are effective in removing arsenate and chromate in wastewater.

Keywords : Modacrylic fibers, Ion exchange fibers, Arsenate, Chromate, Heavy metals, Wastewater treatment

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1. Introduction

1.1. Background

Arsenic (As) is a toxic contaminant that causes serious health problems and human mortality especially in Asian countries such as Bangladesh and India (Richard et al., 1991; Zhitkovich, 2011; An et al., 2015; Wang et al., 2014; Dixit et al, 2003). Groundwater in Bangladesh that used for public water supply are commonly polluted with arsenic, which harms millions of Bangladeshis' health (Nickson et al., 1998). For arsenic, the WHO recommends a maximum contaminant level of 0.01 mg/L for drinking water. Arsenic contamination of drinking water resources occurs through geochemical reactions, pesticide applications, and mining activities (An et al., 2015). Among the different valance states (−3 to 5), most arsenic exists as As(III) and As(V) in water; As(III) occurs in reducing conditions, while As(V) is predominant in oxidizing environments. It is known that As(III) is more toxic and mobile than As(V) (Bang et al., 2004; Giménez et al., 2007).

Meanwhile, Chromium (Cr) is a toxic metal that causes various health problems including hemorrhage, skin dermatitis, and cancer in the digestive tract and lung (Zhitkovich, 2011). The contamination of

water resources by chromium is a serious environmental problem around the world. Guiyu, China is one of the regions polluted with chromium. River sediments samples of Guiyu had a much higher concentration of chromium than soil-pollution-risk threshold of U.S. environmental protection agency (Wong et al., 2007; Li et al., 2008). Chromium contamination of surface water and groundwater occurs by wastewater discharge from electroplating, leather tanning, textile, paint, and dyeing industries (Richard and Bourg, 1991). Among its possible oxidation states (-2 to +6), chromium mainly occurs as trivalent Cr(III) and hexavalent Cr(VI) in aquatic environments. Cr(III) is relatively stable and less dangerous due to its low aqueous solubility, whereas Cr(VI) is extremely water soluble and highly toxic (Richard and Bourg, 1991). The World Health Organization has recommended a guideline of 0.05 mg/L for Cr(VI) in drinking water, whereas the United States Environmental Protection Agency regulates a maximum allowable level of 0.1 mg/L for total chromium in drinking water (Bhaumik et al., 2012; Huang et al., 2012).

Ion exchange is a water treatment process used for removing dissolved ions in aqueous phase through the exchange with ions on the solid phase. Basically, two types of ion exchange media, such as ion

exchange resins and ion exchange fibers have been used in water treatment practices. Ion exchange fibers have advantages over ion exchange resins, including larger specific surface area, higher ion exchange capacity, and rapid absorption/desorption rate (Kosandrovich and Soldatov, 2012). Numerous researchers have used anion exchange fibers for the removal of As(V) and Cr(VI) from aqueous solutions (Kong et al., 2014; Dai et al., 2015; Wang et al., 2015; Zhen et al., 2016; Lee et al., 2017; Gao et al., 2017). However, a very limited studies have been performed on As(V) and Cr(VI) removal from wastewater using anion exchange fibers. The objective of this study was to characterize modacrylic anion exchange fibers in the removal of As(V) and Cr(VI) from synthetic water and wastewater. The ion exchange fibers used in the experiments were acrylonitrile-vinyl chloride copolymer fibers; these are types of the modacrylic fibers, denoting modified acrylic fibers made from acrylonitrile (Nesteronok and Soldatov, 2011; Lee et al., 2016). Energy dispersive X-ray spectrometer (EDS), Fourier-transform infrared spectrometer (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses also performed to characterize the anion exchange fibers in the removal of As(V) and Cr(VI). Batch experiments were performed to examine the effects of solution pH, regeneration,

and initial As(V) and Cr(VI) concentration on the removal of the toxic anions from aqueous solutions. Column experiments were performed to remove arsenate and chromate in wastewater.

1.2. Objective

The objective of this study is to investigate arsenate and chromate ion removal from aqueous solution using commercial anion exchange fibers and to apply the anion exchange fibers to treat wastewater containing the toxic heavy metals.

2. Literature Review

2.1. Cr(VI) removal using anion exchanger

Numerous research groups have used anion-exchange resins for Cr(VI) removal (Sengupta et al., 1986; Galan et al., 2005; Mustafa et al., 1997; Neagu et al., 2003; Lin et al., 2003; Marshall et al., 2006). For instance, Mukhopadhyay et al. (2007) have used commercial IRA-900 and A-100 anion-exchange resins to remove Cr(VI) from contaminated groundwater. Shi et al. (2009) have performed batch experiments to remove Cr(VI) from electroplating wastewater using commercial D301, D314, and D354 anion-exchange resins. El-Moselhy et al. (2015) have applied IRA-900 and carminic acid-modified IRA-900 anion-exchange resins for the removal of Cr(VI) from synthetic and real wastewater samples. Anion exchange fibers have several advantages over anion-exchange resins, such as a faster adsorption–desorption rate and a higher anion-exchange capacity (Henryk et al., 2016). Several studies have been reported in the literature for Cr(VI) removal from synthetic solutions by anion-exchange fibers, including polypyrrole–polyaniline nanofibers (Bhaumik et al., 2012), polypropylene-based fibers (Wang et al., 2012), polyphenylene sulfide-

based fibers (Huang et al., 2012), and porous carbon-based hybrid fibers (Zheng et al., 2016). However, a very limited number of studies have been performed on Cr(VI) removal from industrial wastewater using anion-exchange fibers. Dai et al. (2015) have used polypropylene based anion-exchange fibers to remove Cr(VI) from electroplating wastewater. Lee et al. (2016) have examined the removal and recovery of Cr(VI) from industrial plating wastewater by anion-exchanger Kanecaron^{TM} SA fibers under batch conditions. These studies showed that anion-exchanger fibers could be successfully applied for the removal and recovery of Cr(VI) from industrial wastewater.

2.2. As(V) removal using anion exchanger

Dominguez et al. (2003) synthesized anion exchange fibers using a vinylbenzyl chloride copolymer as a precursor and fiberglass fiber as a substrate through amine functionalization and hydrochloric acid treatment for As(V) removal from aqueous solutions. Vatutsina et al. (2007) prepared hybrid fibrous sorbents through the impregnation of polypropylene- based and polyacrylic-based ion exchange fibers with hydrated ferric oxides for As(V) removal from drinking water. Smith et

al. (2015) impregnated polypropylene-based ion exchange fibers with hydrated ferric oxides for As(V) removal. These studies showed that the fibrous anion exchangers could be successfully applied for decontamination of As(V) from water. Furthermore, studies related to application of fibrous ion exchangers to As(V) removal from arsenic wastewater are scarce.

2.3. Heavy metal removal by ion exchange fibers

There have been many researches to remove toxic heavy metals using ion exchange fibers. Kong et al. (2014) removed Cr(VI) by 2-(dimethylamino)ethyl methacrylate functioned and 1-bromoalkanes modified quaternary ammonium fibers. Kavaklı et al. (2014) tried to remove As(V) using quaternized dimethylaminoethyl methacrylate strong base anion exchange fibers. Dai et al. (2015) used weak anion exchange fiber with polyamine group to remove Cr(VI) ions. Ntimbani et al. (2015) remove Cu(II) in presence of other ions including Co(II), Ni(II), Zn(II), Mn(II), Mg(II) by polyacrylic weak-cation exchange fibers. Wang et al. (2015) removed Cr(VI) ions by strong alkaline anion

exchange fibers. Zheng et al. (2016) used hybrid strong anion exchange porous carbon fibers to remove Cr(VI) ions. Lee et al. (2017) applied acrylic ion exchange fibers to remove As(V). Tu et al. (2017) synthesized Chitosan-rectorite nanospheres immobilized polystyrene fibers and used them to remove Cu(II) ions. Gao et al. (2017) made ultra-high molecular weight polyethylene fibers and applied them to remove Cr(VI). These studies indicated that ion exchange fibers can be successfully applied to remove various heavy metals from aqueous solutions.

3. Materials and Methods

1. Preparation and characterization of anion exchange fibers

Three anion exchange fibers (made by Kanecaron^{TM} in Japan, product name: KC31, SA, SA2) were used for the experiments in this study. The digital images of these fibers are shown in Fig. 1.

Field emission scanning electron microscopy (FESEM, Supra 55VP, Carl Zeiss, Oberkochen, Germany) and Energy dispersive X-ray spectrometer (EDS) analysis were conducted to observe the surface of the fibers and investigate atomic ratio of the surface.

Fourier transform infrared spectroscopy (FTIR) was used to inquire functional groups in the fibers and compare the functional groups of pristine fibers with those of As(V) adsorbed fibers and Cr(VI) adsorbed fibers.

Anion exchange capacities of the fibers were quantified by the methods described in Neagu *et al*., 2010. The anion exchange fibers were prepared into two groups. In the first group, the pristine KC31, SA, and SA2 fibers were prepared as they were produced, whereas the fibers were spiked in 1 M hydrochloric acid (HCl) solution (dose: 1 g/L)

for 6 hours and dried at 65 ℃ in an oven (ThermoStable SOF-W 155, Daihan Scientific, Seoul, Korea) in the second group. A 0.3 g sample of the each fiber of two groups was soaked in 300 mL of 5 % sodium sulfate (Na_2SO_4) solution and shaken for 6 hours at 30 ℃. The fibers were separated from solution after the stirring. Chlorine ion (Cl^-) concentrations of residual Na_2SO_4 solutions were measured by ion chromatography (IC) (ICS-3000, Dionex, Sunnyvale, CA, USA). By the experiments using first group of fibers, the number of functional groups containing chloride ions (Cl^-) in certain amount of fibers was come out. On the other hand, the number of functional groups was quantified by the experiments using second group of fibers.

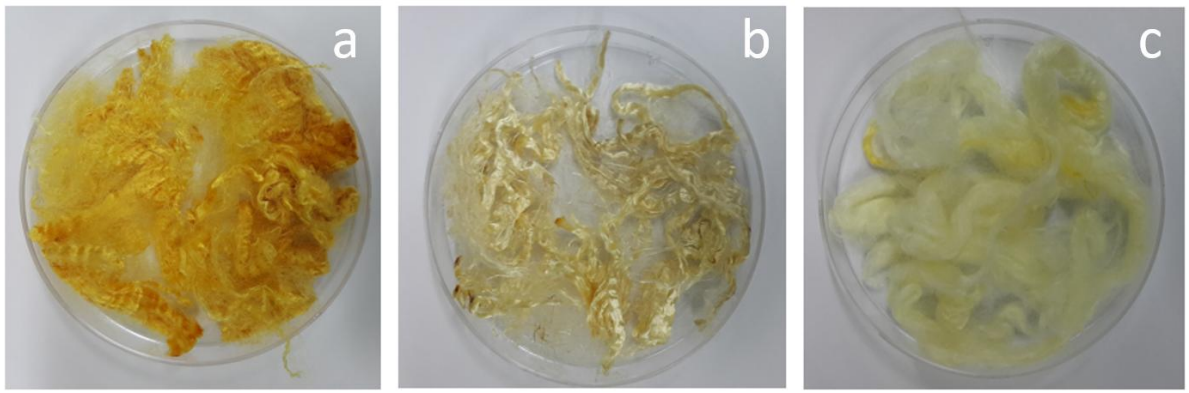

Fig. 1. Digital images of anion exchange fibers:
(a) KC31; (b) SA; (c) SA2

2. As(V) removal from synthetic water

2.1. Synthetic water experiments

All experiments were conducted in batch condition using synthetic water. The stock solution of As(V) (1,000 ppm as As) was prepared by sodium arsenate dibasic heptahydrate (Na_2HAsO_4, ACS reagent, Sigma-Aldrich, St. Louis, MO, USA) dissolved in deionized water. The solutions of desired As(V) concentration was prepared by diluting the stock solution. Batch tests were performed in duplicate using 300 mL of As(V) solutions in 500 mL flask. All batch experiments were performed at a temperature of 30 °C. The fiber dose was always 1.0 g/L at all batch tests.

2.2. Effect of pH

For the first experiments conducted to determine the effect of pH on the removal of As(V), 10 mg/L of As(V) solutions with different pH (2-12) were prepared. The pH of solutions was adjusted by 0.1 M HCl and 0.1 M NaOH. Measurements of the pH value were taken by glass electrode pH meter (Orion, model 720A). Each fibers were soaked in the solutions, shaken at 150 rpm for 6 hours using a shaking incubator (Daihan Science, Seoul, Korea), and separated from the solutions. The

As(V) concentrations of the solution after the reaction were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima-4300, PerkinElmer, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) (Sigma Probe, Thermo VG, East Grinstead, UK) analysis was conducted to the anion exchange mechanism of anion exchange fibers.

2.3. Effect of As(V) concentration

The second experiments were carried out to examine the effect of initial As(V) concentration. As(V) solutions of various concentrations (10, 50, 100, 200, 500 mg/L) were prepared. The solutions were made without adjusting the pH (initial pH 7.5-8.6) and reacted with anion exchange fibers for 6 hours.

2.3. Effect of contact time

The third experiments were conducted to investigate the influence of contact time. Anion exchange fibers were spiked at 10 mg/L of As(V) solution for 5, 10, 15, 30, 60, 120, 180 minutes. Consulting the results of pH experiments, initial pH of As(V) solutions for KC31 was adjusted to 3 and that for SA, SA2 was adjusted to 10.

2.4. Regeneration of ion exchange fibers

The last experiments were to observe the As(V) adsorption changes as fibers were regenerated. Fibers were immersed in 10 mg/L of As(V) solutions (initial pH 7.5) for 6 hours. After the adsorption, the fibers reacted with 0.1 M NaCl solutions over 3 hours for regeneration of the anion exchange fibers. The regenerated fibers were slightly washed and dried at 65 °C in an oven for 2 hours. The above adsorption-desorption processes were repeated five times.

3. As(V) removal from mining wastewater

The mining wastewater was produced from a gold smelting process. Gold ores were heated by microwave in the smelting process, from which arsenic vapor was generated. Nitric acid (HNO_3) solution (1.0 M) was used to trap gaseous arsenic.

The ions included in the mining wastewater were analyzed by ICP-AES and IC. The characteristics of the wastewater obtained from the analysis were shown in Table 1. Most importantly, As(V) concentration of the wastewater was 5,600 mg/L and pH of that was 2.9.

Column experiment was carried out to remove As(V) from mining wastewater. From the results of pH experiments, KC31 was thought to be suitable to remove As(V) at pH 2.9 and chosen to be used at this experiment. KC31 fibers (13.92 g) were packed in Plexigals column (inner diameter: 2.5 cm, height: 10 cm). Before the mining wastewater fed, the column had been saturated with deionized water injected from the bottom of column. Deionized water and wastewater ran steadily by a peristaltic pump (QG400, Fluid Metering Inc., Syosset, NY, USA). The effluent from the column was collected every ten minutes after the wastewater injection by an auto-collector (Retriever 500, Teledyne, City of Industry, CA, USA). As(V) concentration of collected samples

were measured. The condition of the column experiment was presented in Table 2.

Table 1. Characteristics of mining wastewater used in the column experiments

Ion	As	Cr	Br	Cu	Zn	K	Cl	Na	NO_3	PO_4	SO_4	pH
Concentration (mg/L)	5580	2800	1150	324	4830	2310	362	4880	27600	479	1130	2.9

Table 2. Experimental conditions of column experiment for mining wastewater

Parameter	Value
Column diameter (cm)	2.5
Column length (cm)	10
Weight of fibers (g)	13.92
Pore volume (mL)	39.27
Porosity	0.80
Packing fraction (%)	20
Flow rate (mL/min)	1.0
Flow direction	Upflow

4. Cr(VI) removal from synthetic water

4.1. Synthetic water experiments

The Cr(VI) stock solution (1,000 ppm as Cr) was prepared by potassium dichromate ($K_2Cr_2O_7$, Sigma-Aldrich, St. Louis, MO, USA). All batch tests were performed in duplicate at a temperature of 30 ℃. Cr(VI) solution of certain concentration needed for batch tests, 300 mL of diluted solutions filled in 500 mL flask were used. The fiber dose was always 1.0 g/L in every batch tests.

4.2. Effect of pH

To examine the effect of pH on the removal of Cr(VI), anion exchange fibers were added to 50 mg/L of Cr(VI) solutions with different pH (2-12). The pH of these solutions was adjusted by 0.1 M HCl and 0.1 M NaOH. Each fibers with Cr(VI) solutions were shaken at 150 rpm for 6 hours and filtered from the solutions. The Cr(VI) concentrations of the residual solution after the filtering were analyzed by ICP-AES.

4.3. Effect of Cr(VI) concentration

To observe the effect of initial Cr(VI) concentration, the fibers were soaked in various concentrations of Cr(VI) solutions (10-1000 mg/L). The pH of these solutions was not adjusted (initial pH 4.3-5.1).

Reaction time of the solutions with the fibers was 6 hours.

4.4. Effect of contact time

To investigate the influence of contact time, the fibers were spiked at 10 mg/L of Cr(VI) solution for 5, 10, 15, 30, 60, 120, 180 minutes. The pH of these solutions was also not adjusted (initial pH 5.1).

4.5. Regeneration of ion exchange fibers

Regeneration experiments were conducted. In adsorption process, 50 mg/L of Cr(VI) solutions were reacted with fibers for 3 hours. After the adsorption, to regenerate the Cr-sorbed anion exchange fibers, the fibers were soaked in 1.0 M NaCl solutions for 3 hours. After that, the fibers were slightly washed and dried at 65 °C in an oven for 2 hours. The above adsorption-desorption processes were repeated five times.

5. Cr(VI) removal from chromium-plating rinse water

Chromium-plating rinse water used in this experiments was obtained from a plating plant located in Ansan, Republic of Korea.

The concentrations of ions in the mining wastewater were measured

by ICP-AES and IC. Furthermore, using the diphenylcarbazide method by UV/Vis spectrophotometer (Helios, Thermo Scientific, Waltham, MA, USA), the concentration of Cr(VI) concentration in the wastewater. As the Cr concentration from ICP-AES analysis represents only total Cr content regardless of the valence of Cr, information about the proportion of Cr(VI) in total Cr concentration can be obtained by diphenylcarbazide methods. The characteristics of the chromium-plating rinse water were presented in Table 3. Cr(VI) concentration of the wastewater was 1178.8 mg/L and Cr(III) was not found in the water.

Column experiment was performed to remove Cr(VI) from chromium-plating rinse water. As the maximum removal capacity for Cr(VI) of KC31 was the largest of three anion exchange fibers, KC31 was used in this experiments. The condition of column for chromium-plating rinse water were similar with that for mining wastewater except the flow rate (0.5 and 1.0 mL/min for chromium wastewater). The condition of the column experiment was presented in Table 4

Table 3. Characteristics of chromium-plating rinse water used in the column experiments

Ion	Cr(VI)	Cr(III)	Cu	Pb	Zn	Ni	Ca	Mn	Fe	Mg	Na	NH_4	SO_4	pH
Concentration (mg/L)	1180	0.00	5.40	0.36	1.70	17.0	1160	0.04	2.73	102	161	29.7	257	1.8

Table 4. Experimental conditions of column experiment for chromium-plating rinse water

Parameter	Value
Column diameter (cm)	2.5
Column length (cm)	10
Weight of fibers (g)	13.92
Pore volume (mL)	39.27
Porosity	0.80
Packing fraction (%)	20
Flow rate (mL/min)	0.5, 1.0
Flow direction	Upflow

6. Data analysis

All of model were fitted using the solver function in Microsoft Excel 2013. The parameters of models were determined by nonlinear regression. The coefficients of determination coefficient (R^2), chi-square coefficient (χ^2), and sum of the absolute errors (SAE) were used to evaluate model fitting to equilibrium and kinetic data. The following equations were used to calculate the coefficients:

$$R^2 = \frac{\sum_{i=1}^{m}(y_c - \bar{y_e})_i^2}{\sum_{i=1}^{m}(y_c - \bar{y_e})_i^2 + \sum_{i=1}^{m}(y_c - y_e)_i^2} \quad (1)$$

$$\chi^2 = \sum_{i=1}^{m}\left[\frac{(y_e - y_c)^2}{y_c}\right]_i \quad (2)$$

$$\text{SAE} = \sum_{i=1}^{m}|y_c - y_e|_i \quad (3)$$

The equilibrium data were analyzed using the nonlinear isotherm models of Langmuir, Freundlich, and Redlich-Peterson. The following equations represent the isotherm models:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (6)$$

Where q_e indicates the amount of contaminant adsorbed at equilibrium, C_e the equilibrium concentration of contaminant in the aqueous solution, Q_m the maximum adsorption capacity, K_L the Langmuir constant related to the affinity of the binding sites, K_F the Freundlich constant related to the adsorption capacity, 1/n the Freundlich constant related to the adsorption intensity, K_R the Redlich-Peterson constant related to the adsorption capacity, a_R the Redlich-Peterson constant related to the affinity of the binding sites, and g the Redlich-Peterson constant related to the adsorption intensity.

The kinetic data were fitted by the nonlinear pseudo first-order, pseudo second-order, and elovich model. The following equations

$$q_t = q_e(1 - \mathrm{e}^{-\mathrm{k}_1 t}) \quad (7)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (8)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (9)$$

indicate the coefficients:

Where q_t indicates the amount of contaminant adsorbed at time t, q_e the amount of contaminant adsorbed at equilibrium, k_1 the pseudo first-order rate constant, k_2 the pseudo second-order rate constant, α the initial adsorption rate constant and β the Elovich adsorption constant.

The results of column experiments were fitted by nonlinear forms of fixed-bed kinetic sorption models including Bohart-Adams model, Clark model, and Modified dose-response model. The following

$$\frac{C_t}{C_0} = \frac{e^{k_{BA}C_0 t}}{e^{k_{BA}N_0\frac{Z}{U}} - 1 + e^{k_{BA}C_0 t}} \tag{10}$$

$$\frac{C_t}{C_0} = \left(\frac{1}{Ae^{-rt} + 1}\right)^{\frac{1}{n-1}} \tag{11}$$

$$\frac{C_t}{C_0} = 1 - \frac{1}{\left(\frac{C_0 Qt}{q_0 M_f}\right)^a + 1} \tag{12}$$

equations indicate the coefficients:

Where k_{BA} indicates the rate constant of Bohart-Adams model, N_0 the removal capacity, Z the bed depth, U the linear flow velocity, C_0 the contaminant concentration in the influent, A the Clark model constant, r the Clark model rate constant, n the Freundlich constant, Q the flow

rate, q_0 the removal capacity per unit mass of fiber, Mf the mass of fiber packed into the column, and a the modified dose-response model constant.

4. Results and Discussion

1. Characterization of anion exchange fibers

1.1. FESEM, EDS

FESEM images of KC31, SA, and SA2 is shown in Fig. 2. Three fibers have cylindrical shape. Diameter of each fibers was 21.79 ± 6.11 μm for KC31, 23.52 ± 6.56 μm for SA, and 26.23 ± 4.65 μm for SA2. The EDS spectra shown in Table 5 represented that the fibers mainly consist of carbon, nitrogen, oxygen, and chlorine. It could be verified that the frame of these fibers was modacrylic, copolymer of acrylonitrile (C_3H_3N) and vinyl chloride (C_2H_3Cl) from the elementary composition obtained by EDS analysis.

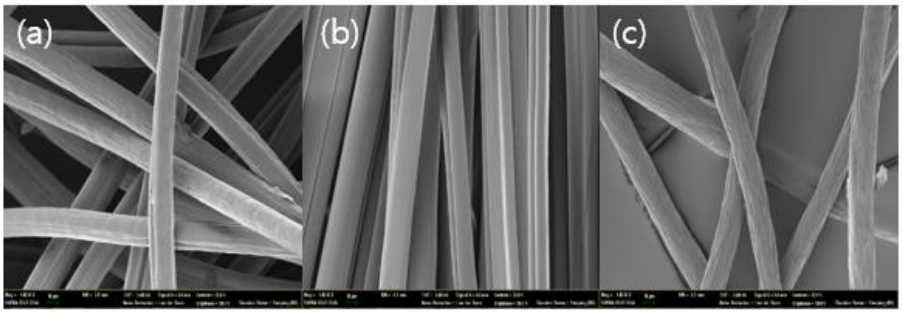

Fig. 2. FESEM images of anion exchange fibers:
(a) KC31; (b) SA; (c) SA2

Table 5. Atomic ratio of anion exchange fibers from EDS analysis

Element	KC31	SA	SA2
C (mol %)	64.89	69.03	64.16
N (mol %)	20.12	10.05	18.13
O (mol %)	13.30	12.01	17.63
Cl (mol %)	1.70	8.91	0.08

1.2. FTIR

The FTIR spectra of three anion exchange fibers are presented in Fig. 3.

Before KC31, SA, SA2 fibers removed As(V) or Cr(VI), C-H vibration peaks appeared at 2933, 2925, 2243 cm^{-1}, respectively (Li et al., 2012). The peaks at 1650, 1653, and 1637 cm^{-1} presented to amide I, and the peaks at 1555, 1556, and 1551 cm^{-1} presented to amide II (Li et al., 2012; Koyama et al., 1973). The peaks at 2239, 2241, and 2243 represented to C≡N bond included in acrylonitrile (Turhan et al., 2010), whereas the peaks at 677, 669, and 677 to C-Cl bond included in vinyl chloride (Ashraf et al., 2008). The peaks at 3294, 3376, and 3249 cm^{-1} corresponded to N-H bond from amine groups, usually acting as functional groups anion exchange fibers (Li et al., 2012).

After the anion exchange fibers removed As(V), there appears the peaks at 830, 843, and 837 cm^{-1} that presented As-O bond of arsenate (Lakshmipathiraj et al., 2006). It indicates three anion exchange fibers successfully adsorbed arsenate.

After the fibers removed Cr(VI), Cr=O peaks at 897, 933, and 938 cm^{-1} appeared, and Cr-O peaks at 772, 755, and 762 cm^{-1} did (Ko et al., 2002; Shin et al., 2004). It represents that the chromate anion were

properly adsorbed to anion exchange fibers after the Cr(VI) removal experiments.

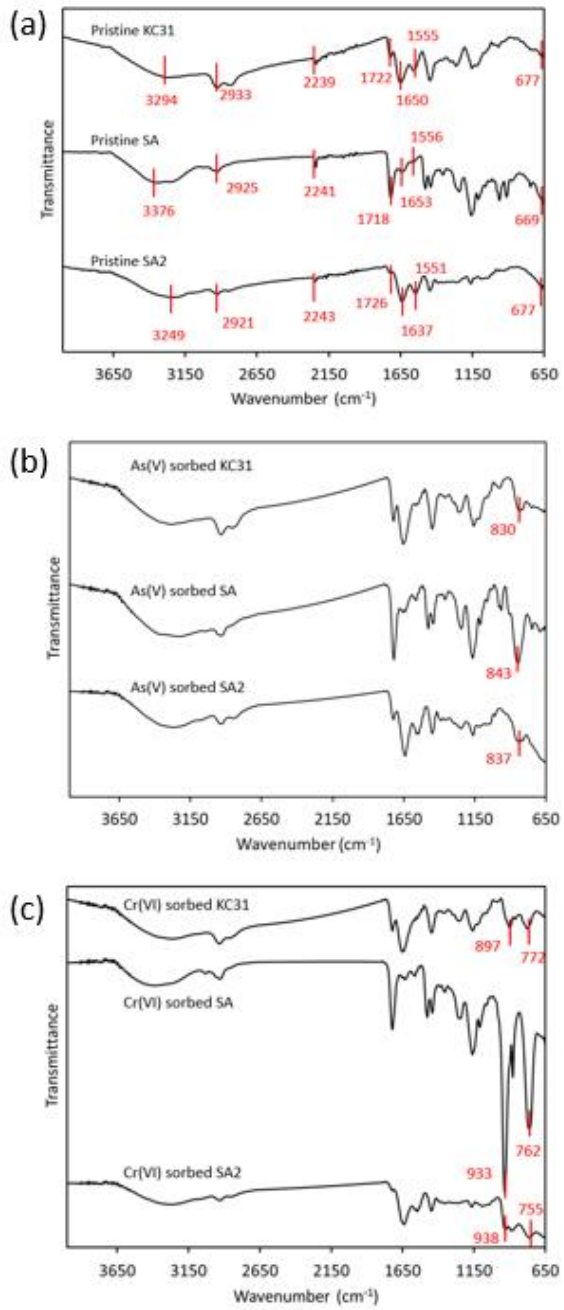

Fig. 3. FTIR spectra of three anion exchange fibers: (a) pristine fibers; (b) fibers after As(V) removal; (c) fibers after Cr(VI) removal

1.3. XPS

The wide scan XPS spectra of the KC31, SA, and SA2 are presented in Fig. 4.

The peaks at 399.2 and 400.5 eV related to C≡N bond from acrylonitrile and C-N bond from amine functional group were observed in case of KC31 (Fig. 5(a)). In case of SA, C≡N and C-N^+ peaks at 399.2 and 402.2 eV appeared without C-N peak (Fig. 5(b)). In case of SA2, there were C≡N, C-N, and C-N^+ peaks (Fig. 5(c)). The XPS data and precedent results from anion exchange capacity experiments had something in common, verifying the prior analysis.

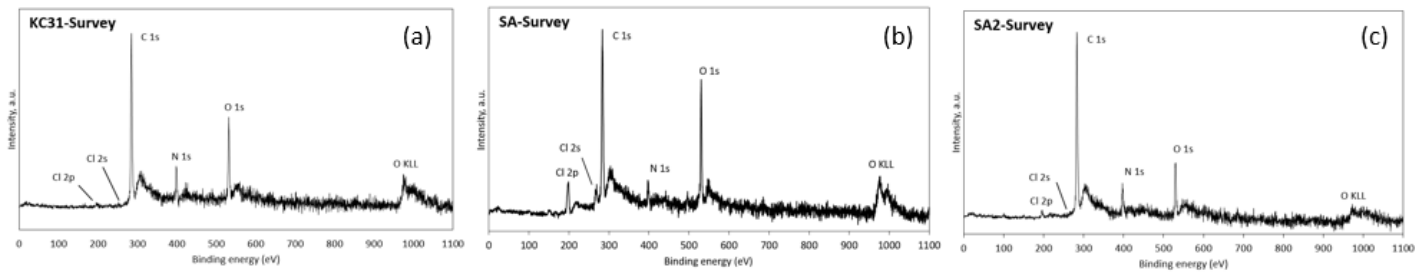

Fig. 4. Wide scan XPS spectra of anion exchange fibers: (a) KC31, (b) SA, (c) SA2

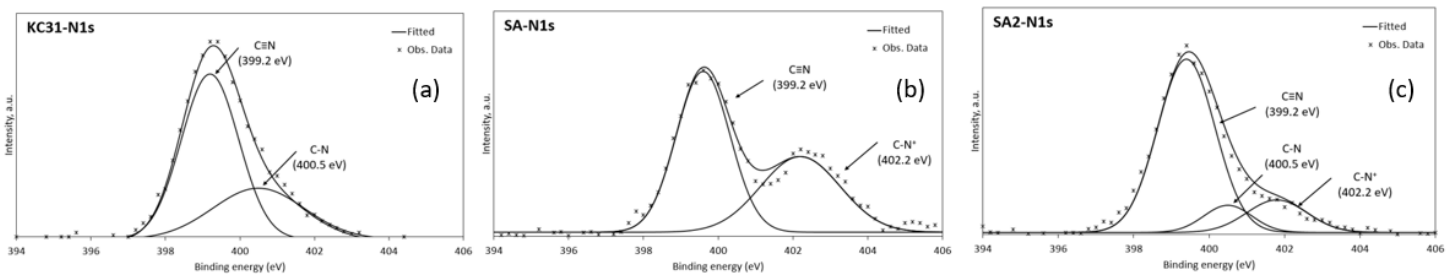

Fig. 5. N1s regions high-resolution scan XPS spectra of anion exchange fibers: (a) KC31; (b) SA; (c) SA2

1.4. Anion exchange capacity

The results from two separate experiments to examine the number of functional groups containing chloride ions (Cl^-) and the total number of functional groups were shown in Fig. 6. KC31 has the largest amount of functional groups (4.70 mmol/g), none of which contain chloride ions. SA has the smallest amount of functional groups (1.15 mmol/g), all of which contain chloride ions. SA2 has 2.65 mmol/g of functional groups, about half of which contain chloride ions (1.34 mmol/g).

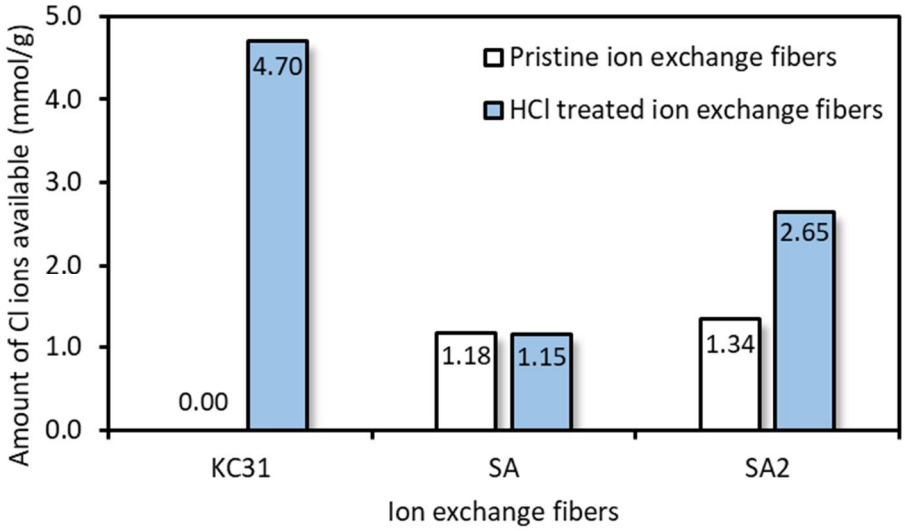

Fig. 6. Amount of chlorine (Cl) ions available on the ion exchange sites of KC31, SA, SA2

2. As(V) removal from synthetic water

2.1. Effect of pH

The effect of initial solution pH on the removal of As(V) by anion exchange fibers was shown in Fig. 7. It appears that the initial pH changes of As(V) solutions strongly influenced the removal of As(V) by the fibers.

In case of KC31, it could remove a little amount of As(V) in the solution (1.428 mg/g) at a pH 2. The removal capacity of KC31 dramatically increased at a pH 4 (9.480 mg/g) and started to decrease slowly as the pH increased. KC31 could hardly remove As(V) at a solution pH 12.

In case of SA and SA2, the pH dependency of As(V) removal was very different from KC31 at the pH range from 4 to 10. For SA, the removal capacity increased gradually from 5.769 to 9.740 mg/g with increasing pH from 4 to 10. At the same pH range, the removal capacity for SA2 also increased from 5.319 to 8.391 mg/g.

From the results of anion exchange capacity experiments, KC31 has no Cl ions available on the ion exchange sites, whereas SA and SA2 has Cl ion available. This indicates that amine groups of pristine KC31 are not protonated at all. On the other hand, amine groups of SA are all

protonated and that of SA2 are half protonated. Amine groups can't properly acted as ion exchange sites before they get protons (H^+) and have positive charge.

In case of KC31, the pH dependency of As(V) removal could be related to whether the amine groups are protonated or not. At pH 2, there are many protons that can protonate the amine groups of KC31. Anion exchange sites of KC31 began to work at pH 2, but amount of As(V) removal was insignificant. It can be related to the speciation of As(V) in highly acidic pH; H_3AsO_4 is major ionic form at pH 2 as shown in Fig. 8 and it couldn't be adsorbed due to its electrical neutrality. At pH 4, major ionic form of arsenate become H_2AsO4^- and protonated amine groups of KC31 could arsenate. As pH increased, the number of protonated functional groups of KC31 gradually decreased. That resulted in decrease of the As(V) removal capacity of KC31 and finally loss of removal capacity at pH 12. Similar findings were appeared in Awual et al. (2008) who demonstrated that the amount of As(V) removal by weak-base anion exchange fibers went down slowly with pH increasing from 3 to 8.

In case of SA and SA2, the pH dependency of As(V) removal was different from KC31 at the pH range from 4 to 10. Since the fibers

already have protonated amine groups and exchangeable Cl ions before they contact with solution, they don't have to obtain protons in solution. It cause that the pH dependency of As(V) removal of these fibers could be mainly related to ionic form of arsenate. At pH 2, H_3AsO_4 is major ionic form of arsenate and it couldn't be adsorbed well. As pH increased from 4 to 10, major arsenate ion in the solution changed from monovalent $H_2AsO_4^-$ to $HAsO_4^{2-}$. The preference of As(V) species to anion exchanger generally become larger as valence of the As(V) is larger as follows; $H_3AsO_4 < H_2AsO_4^- < HAsO_4^{2-} < AsO_4^{3-}$ (An et al., 2005). Due to the preference of divalent ions of fibers, the removal capacity of SA and SA2 is gradually increased as pH increased from 4 to 10. At pH 12 where amine groups of anion exchange fibers lose their proton because of high basicity of solutions, deprotonated SA and SA2 couldn't remove enough As(V) any more. Similar results were found by Jachula and Hubicki (2013) who used polyacrylate and polystyrene based anion exchange resins for As(V) removal.

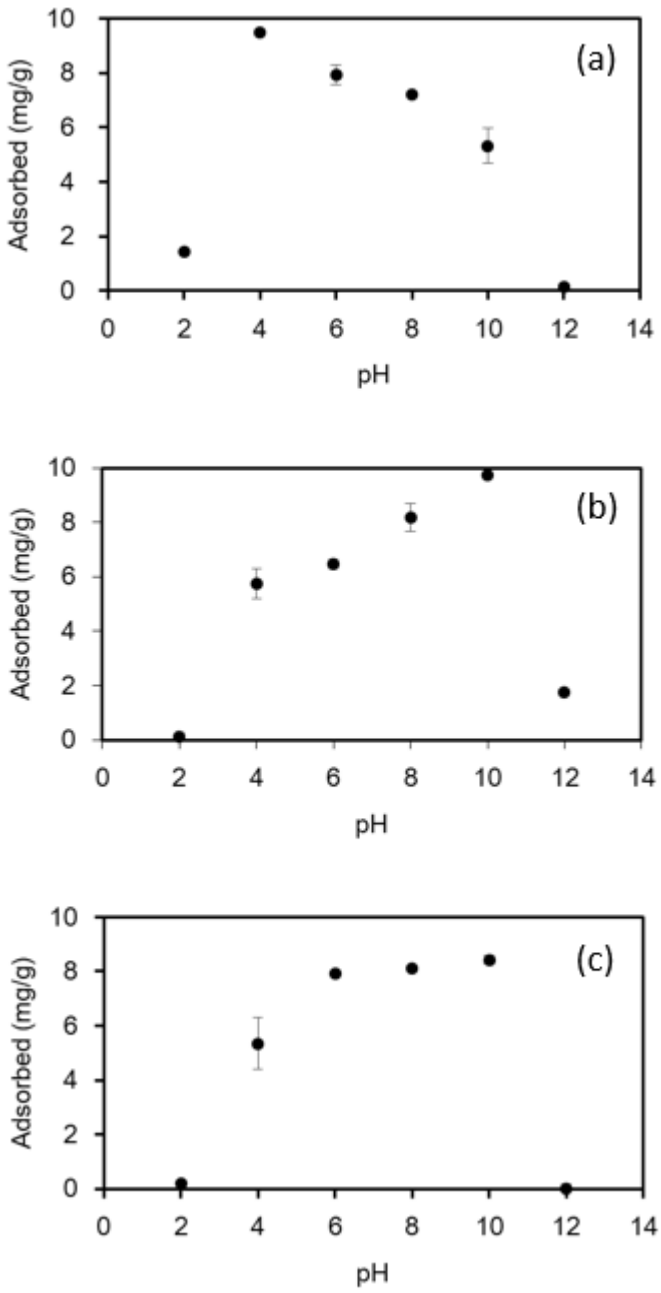

Fig. 7. Effect of solution pH on As(V) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

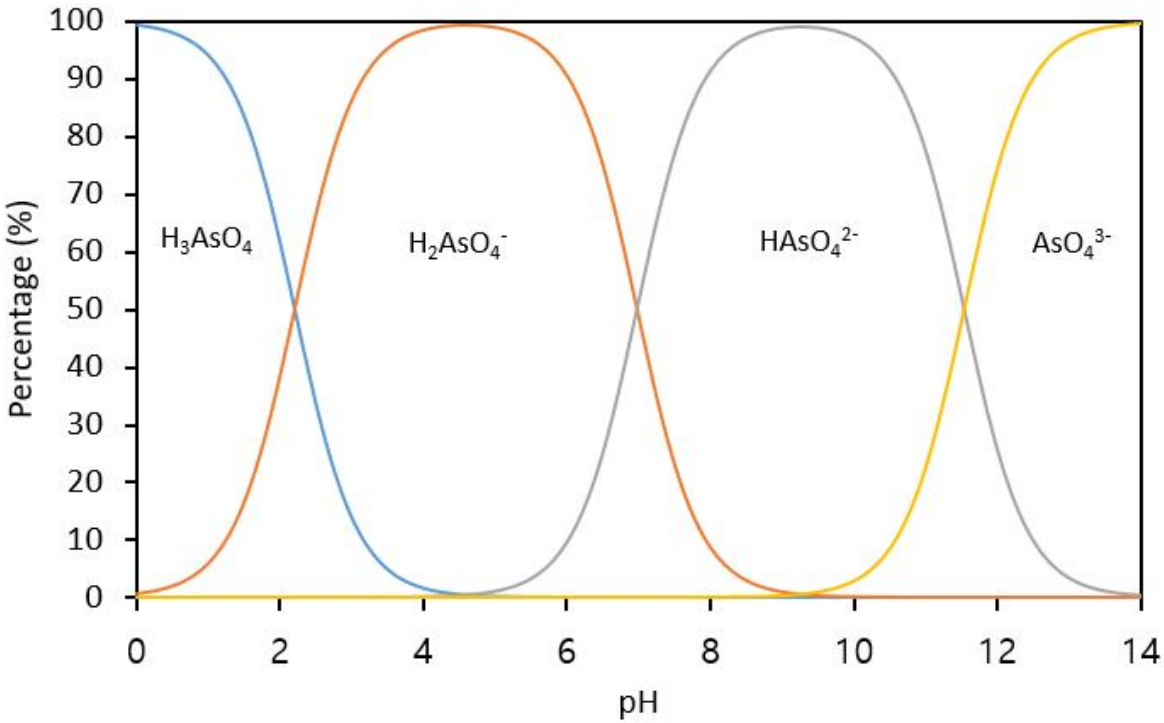

Fig. 8. Distribution of As(V) species as a function of pH

2.3. Effect of As(V) concentration

The effect of As(V) concentration on the As(V) removal by anion exchange fibers along with the model fits was shown in Fig. 9. Model parameters of fitted models are shown in Table 6. The values of R^2, χ^2, and SAE indicated that the Redlich-Peterson isotherm exhibited the best fit to the equilibrium data. The Redlich-Peterson model is a hybrid isotherm that combines the Freundlich and Langmuir models. It can be applied to either homogeneous or heterogeneous systems to explain sorption over a wide range of concentrations (Foo et al., 2010). From the Redlich-Peterson model, the following parameter values were determined: K_R = 4.868–9.116 L g^{-1}, a_R = 0.175–0.553 L mg^{-1}, and g = 0.863–1.000 (Table 7). Unlike the anion exchange capacity of the fibers (SA < SA2 < KC31), the maximum As(V) removal capacity (K_R/a_R) from the Redlich-Peterson model was in an increasing order of SA2 (16.499 mg g^{-1}) < KC31 (20.059 mg g^{-1}) < SA (47.184 mg g^{-1}) under the given experimental conditions (initial As(V) concentration = 5-500 mg L^{-1}, pH range = 7.5–8.6).

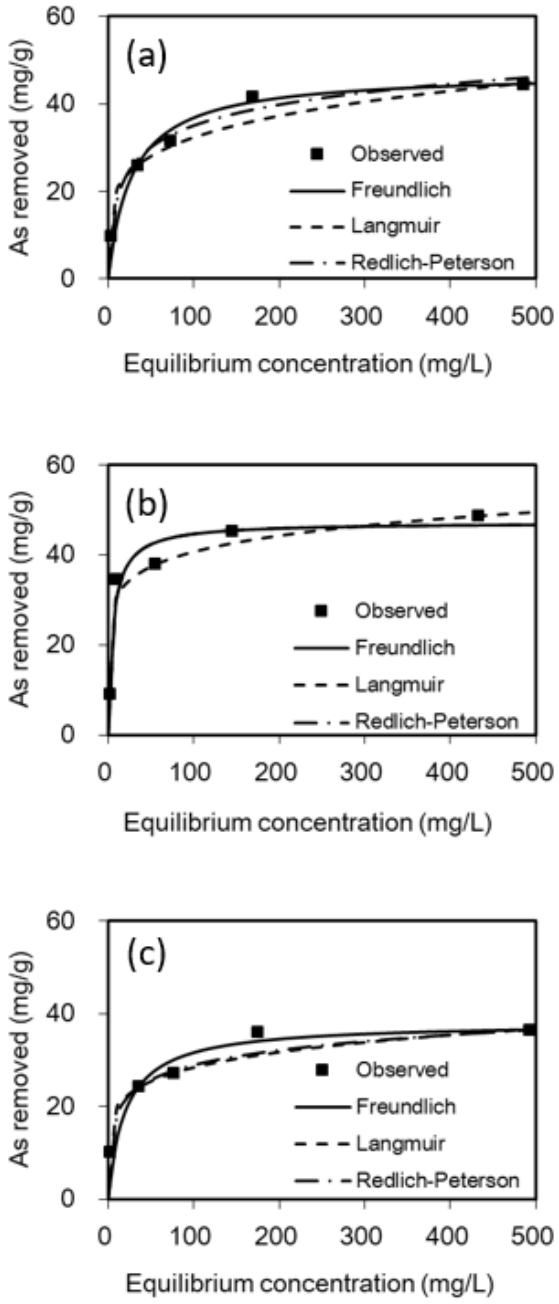

Fig. 9. Equilibrium data and model fits for As(V) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

Table 6. Model parameters of Langmuir, Freundlich, and Redlich-Peterson isotherm model obtained from model fitting to As(V) equilibrium data

	Langmuir isotherm model					Freundlich isotherm model					Redlich-Peterson model					
	Q_m (mg/g)	K_L (L/mg)	R^2	χ^2	SAE	K_F (L/g)	1/n	R^2	χ^2	SAE	K_R (L/g)	a_R (L/mg)	g	R^2	χ^2	SAE
KC31	47.16	0.036	0.981	6.13	8.85	12.6	0.205	0.947	3.24	13.3	4.87	0.243	0.863	0.981	0.455	7.55
SA	47.19	0.174	0.935	2.19	14.8	23.3	0.122	0.820	10.9	23.1	8.24	0.175	1.00	0.935	2.19	14.8
SA2	38.05	0.049	0.957	9.61	11.1	13.7	0.159	0.938	2.74	10.8	9.12	0.553	0.870	0.964	0.662	5.22

2.4. Effect of contact time

The effect of contact time on As(V) removal by anion exchange fibers along with the model fits was shown in Fig. 10. Model parameters of fitted models are aligned in Table 7. The ion exchange reaction reached equilibrium in 30 minutes for all anion exchange fibers. It indicates that anion exchange fibers can use their ability within relatively short time. The pseudo second order model fitted to all the kinetic data well. From the pseudo second order model, the following parameter values were determined: q_e = 8.958-10.05 mg g^{-1}, k_2 = 0.055-0.114 g mg^{-1} min^{-1}.

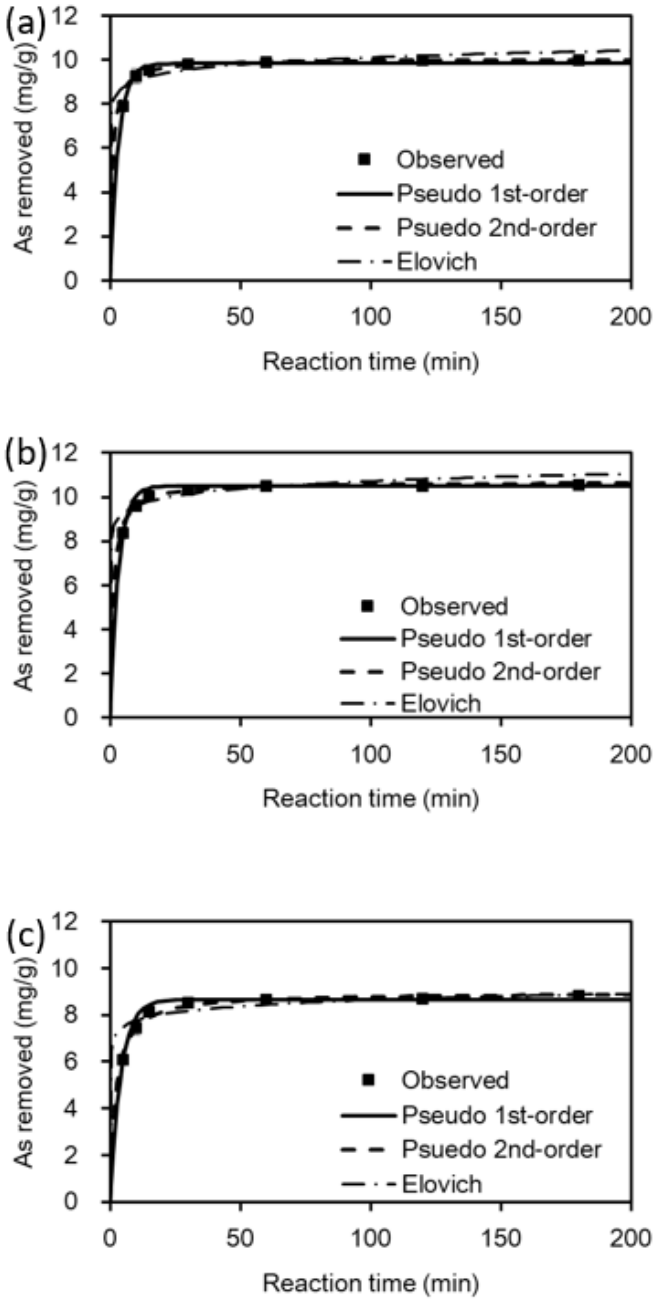

Fig. 10. Kinetic data and model fits for As(V) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

Table 7. Model parameters of pseudo first, pseudo second, Elovich kinetic model obtained from model fitting to As(V) kinetic data

	Pseudo first model					Pseudo second model					Elovich model				
	k_1 (1/min)	q_e (mg/g)	R^2	χ^2	SAE	k_2 (g/mg/min)	q_e (mg/g)	R^2	χ^2	SAE	α	β	R^2	χ^2	SAE
KC31	0.315	9.828	0.960	0.014	0.870	0.114	10.05	0.964	0.052	0.758	2.294×10^7	2.213	0.702	0.119	2.133
SA	0.318	10.49	0.939	0.035	1.031	0.084	10.69	0.977	0.019	0.667	2.338×10^7	2.080	0.727	0.131	2.129
SA2	0.244	8.657	0.951	0.044	1.123	0.055	8.958	0.978	0.021	0.771	2.072×10^7	2.593	0.766	0.295	2.510

2.5. Regeneration of ion exchange fibers

The results of regeneration experiments using anion exchange fibers were presented in Fig. 11. During the five adsorption-desorption cycles, the removal capacity of anion exchange fibers did not change substantially. When the first regeneration process was carried out, the removal capacity of anion exchange fibers was slightly increased. It could be because the protonated amine groups during the As(V) adsorption didn't lose their protons at the desorption process. However, as the regeneration process was repeated, the removal capacity of anion exchange fibers was not increased any more but reached at a certain values.

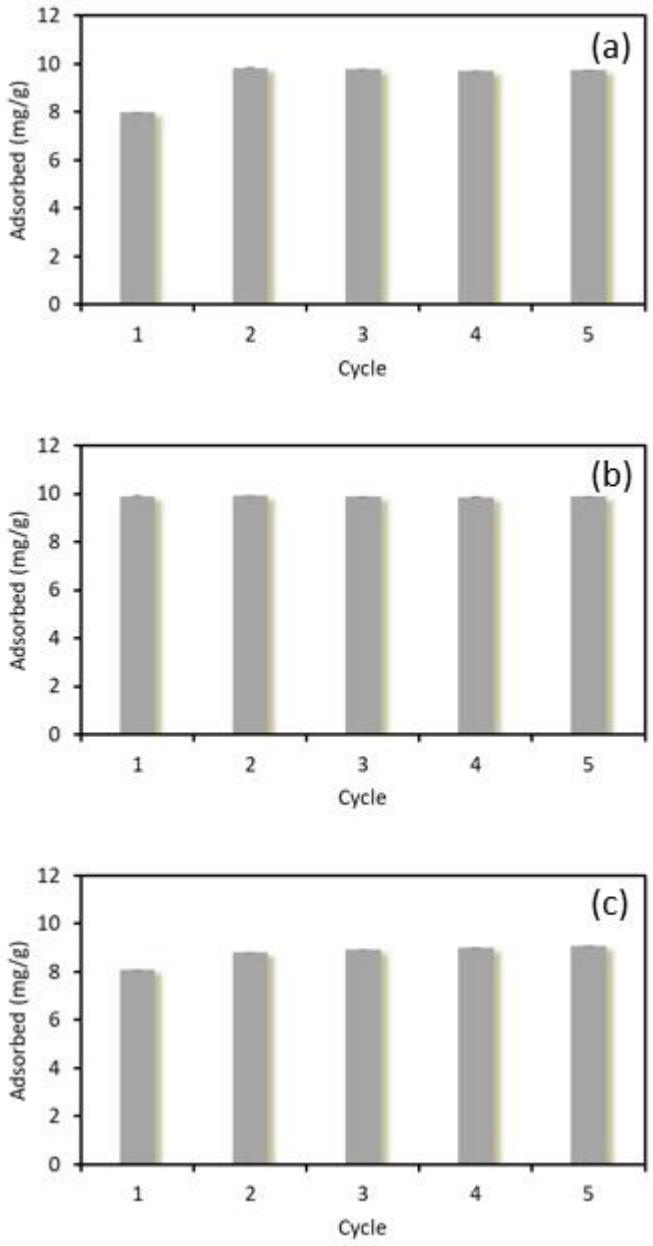

Fig. 11. Regeneration and reuse of anion exchange fibers over five As(V) adsorption-desorption cycles: (a) KC31; (b) SA; (c) SA2

3. As(V) removal from mining wastewater

The breakthrough curves obtained from column experiment to remove As(V) in mining wastewater (Fig. 12). Model parameters of fitted models are shown in Table 8. KC31 could not remove As(V) any more 12 hours after the injection of wastewater. Total amount of adsorbed As(V) from 1070 mL of wastewater was 1145 mg. The results of column experiments represented that maximum As(V) removal capacity of KC31 for the wastewater conditions was 82.29 mg/g. The As(V) removal capacity of Kanecaron fibers from this study was comparable with those of other anion exchangers (12.51-187.1 mg g^{-1}) reported in the literature (Table 9). The modified dose-response model fits the column experiment data well. From the modified dose-response model, the following parameter values were determined: q_0 = 45.75 mg g^{-1}, a = 1.75.

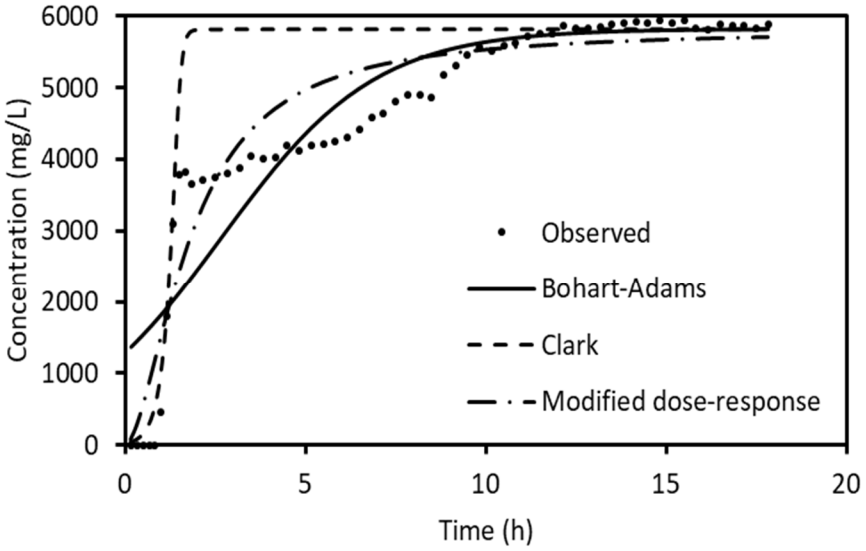

Fig. 12. Breakthrough curves and model fits of fix-bed kinetic sorption models for As(V) removal in mining wastewater by KC31 fibers under flow-through column conditions

Table 8. Model parameters for fixed-bed kinetic sorption models obtained from the breakthrough curves for As(V) removal column experiment

	Bohart-Adams			Clark			Modified dose-response		
	K_{BA} (L/h/g)	N_0 (g/L)	R^2	A	r (1/h)	R^2	a	q_0 (mg/g)	R^2
Values	0.081	28.6	0.840	1.83×10^7	11.3	0.813	1.75	45.75	0.908

Table. 9. As(V) removal capacity of anion exchangers reported in the literature

Anion exchanger	pH	As(V) removal capacity (mg/g)	Reference
Kanecaron fiber KC31	2.9	82.29	This study
Coconut coir pith-based exchanger	7.0	12.51	Anirudhan et al., 2007
Cellulose-based animated exchanger	6.0	187.1	Anirudhan et al., 2010
Polystyrene exchanger (Amberlite IRA 900)	10.0	10.94	Jachula et al., 2013
Polyethylene/polypropylene-based quaternized fibrous exchanger	7.0	83.31	Kavaklı et al., 2014
Purolite A520P/A400	7.0	20.00	Ashraf et al., 2008
Cellulose-based exchanger	6.0	108.7	Lakshmipathiraj et al., 2006
Poly(ethylene mercaptoacetimide) exchanger	2.0	105.6	An et al., 2005
Manganese and iron (hydr)oxide-coated exchanger	5.0	128.2	Gupta et al., 2011
Silica gel-based functionalized exchanger	7.5	13.94	Padungthon et al., 2015

4. Cr(VI) removal from synthetic water

4.1. Effect of pH

The effect of initial solution pH on the removal of Cr(VI) by anion exchange fibers was shown in Fig. X. Initial pH changes in Cr(VI) solutions strongly influenced the removal of Cr(VI) by the fibers.

The removal capacity of three anion exchange fibers was all decreased as pH increased. The Cr(VI) removal capacity of KC31 was the highest at pH 2 (47.89 mg/g). The Cr(VI) removal capacity of SA was the highest at pH 4 (47.16 mg/g). SA2 has highest Cr(VI) removal capacity at pH 6 (48.99 mg/g).

As the solution pH increased, the number of protonated amine groups in anion exchange fibers decreased resulting that the removal of Cr(VI) decreased. Furthermore, because the valence of chromate ions increased (from 1 to 2) as pH increased, divalent form of chromate occupied two amine groups, and the number of anion exchange sites became insufficient.

Similar results were reported by Huang et al. (2012) who demonstrated that the amount of Cr(VI) removal by polyphenylene sulfide-based anion-exchanger fibers went down slowly with pH increasing from 3.5 to 12.

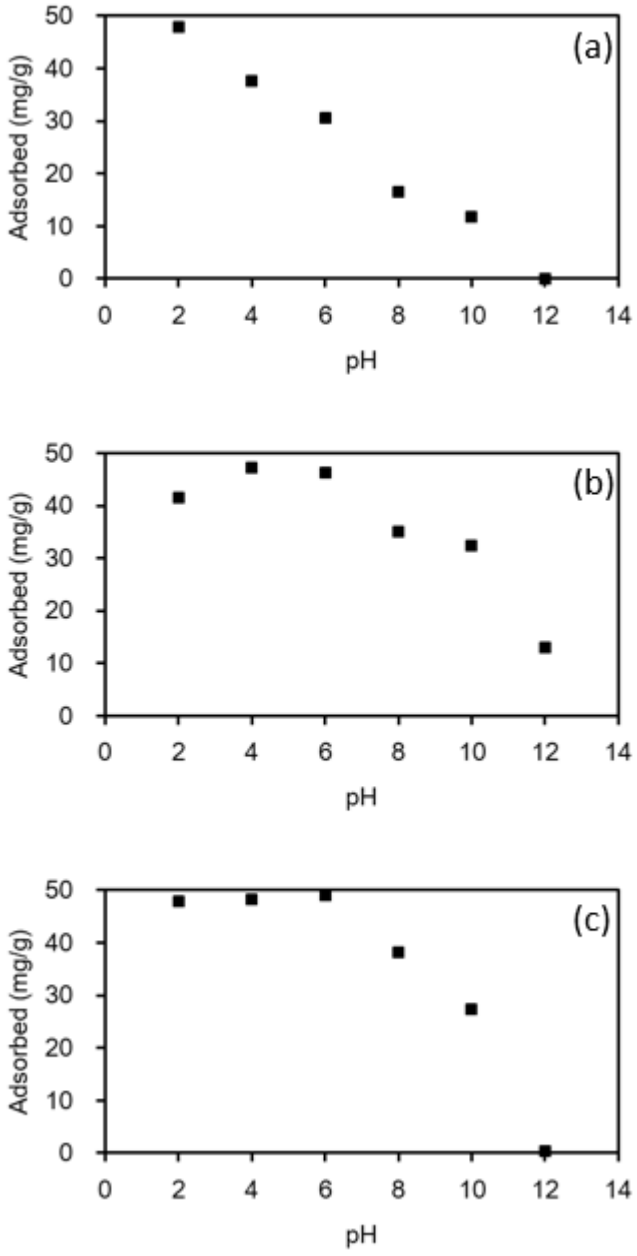

Fig. 13. Effect of solution pH on Cr(VI) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

4.2. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the Cr(VI) removal by anion exchange fibers along with the model fits was shown in Fig. 14. The Cr(VI) removal capacity of Kanecaron fibers from this study was comparable with those of other anion exchangers (19.27-227.0 mg g^{-1}) reported in the literature (Table 11). Model parameters of fitted models are shown in Table 10. The values of R^2, χ^2, and SAE indicated that the Langmuir isotherm exhibited the best fit to the equilibrium data of KC31 and SA, whereas the Freundlich isotherm did to those of SA2. From the Langmuir model, the following parameter values were determined: Q_m = 161.0-250.2 mg g^{-1}, K_L = 0.005-0.010 L mg^{-1}. From the Freundlich model, the following parameter values were determined: K_F = 11.6-24.8 L g^{-1}, 1/n = 0.261-0.426. The maximum As(V) removal capacity (Q_m) from the Langmuir model was in an increasing order of SA2 (161.0 mg g^{-1}) < SA (162.5 mg g^{-1}) < KC31 (250.2 mg g^{-1}) under the given experimental conditions (initial Cr(VI) concentration = 10–1000 mg L^{-1}, pH range = 4.3–5.1).

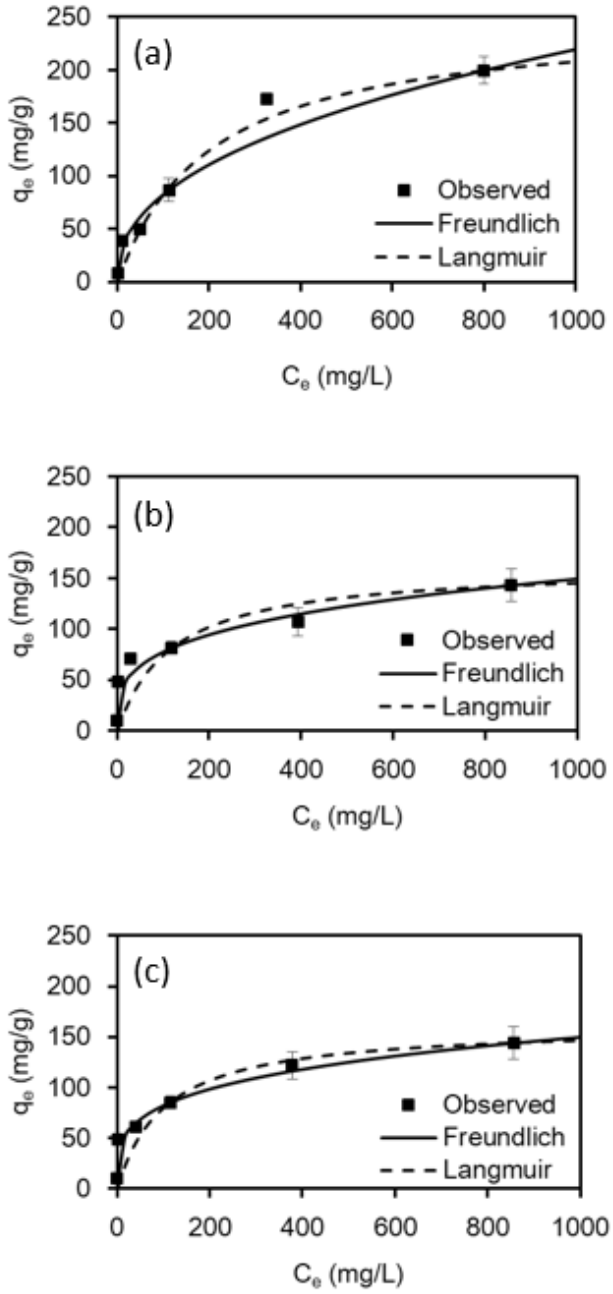

Fig. 14. Equilibrium data and model fits for Cr(VI) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

Table 10. Model parameters of Langmuir and Freundlich isotherm model obtained from model fitting to Cr(VI) equilibrium data

	Langmuir isotherm model					Freundlich isotherm model				
	Q_m (mg/g)	K_L (L/mg)	R^2	χ^2	SAE	K_F (L/g)	1/n	R^2	χ^2	SAE
KC31	250.2	0.005	0.979	66.2	52.3	11.6	0.426	0.959	15.9	60.5
SA	162.5	0.008	0.877	1030	112	20.9	0.285	0.943	27.7	51.8
SA2	161.0	0.010	0.930	2660	78.5	24.8	0.261	0.877	29.3	37.7

Table. 11. Cr(VI) removal capacity of anion exchnagers reported in the literature

Anion exchanger	pH	Cr(VI) removal capacity (mg/g)	Reference
Kanecaron fibers	4.3-5.1	161.0-250.2	This study
Polypyrrole-polyaniline nanofiber	2.0	227	Bhaumik et al., 2012
QAPPS fiber	3.5	166.3	Huang et al., 2012
Amberite IRA-400 resin	3.0	104.0	Mustafa et al., 1997
Ambersep 132 resin	-	92.1	Lin et al., 2003
D354 resin	4.0-5.0	156.3	Shi et al., 2009
Carminic acid-modified Amberite IRA-900 resin	4.0-4.5	19.27	El-Moselhy et al., 2015
SAAEF fiber	1.0	187.7	Wang et al., 2012
Quaternary ammonium chloride RQA resin	3.0	48	Aita et al., 2006

4.3. Effect of contact time

The effect of contact time on Cr(VI) removal by anion exchange fibers along with the model fits was shown in Fig. 15. Model parameters of fitted models are represented in Table 12. The ion exchange reaction reached equilibrium in 15 minutes for SA and SA2 whereas an hour for KC31. The pseudo second order model fitted to the kinetic data of KC31 and SA well, whereas The pseudo first order model did to those of SA2. From the pseudo first order model, the following parameter values were determined: q_e = 8.95-10.2 mg g^{-1}, k_1 = 0.074-0.379 min^{-1}. From the pseudo second order model, the following parameter values were determined: q_e = 9.53-10.3 mg g^{-1}, k_2 = 0.013-0.223 g mg^{-1} min^{-1}.

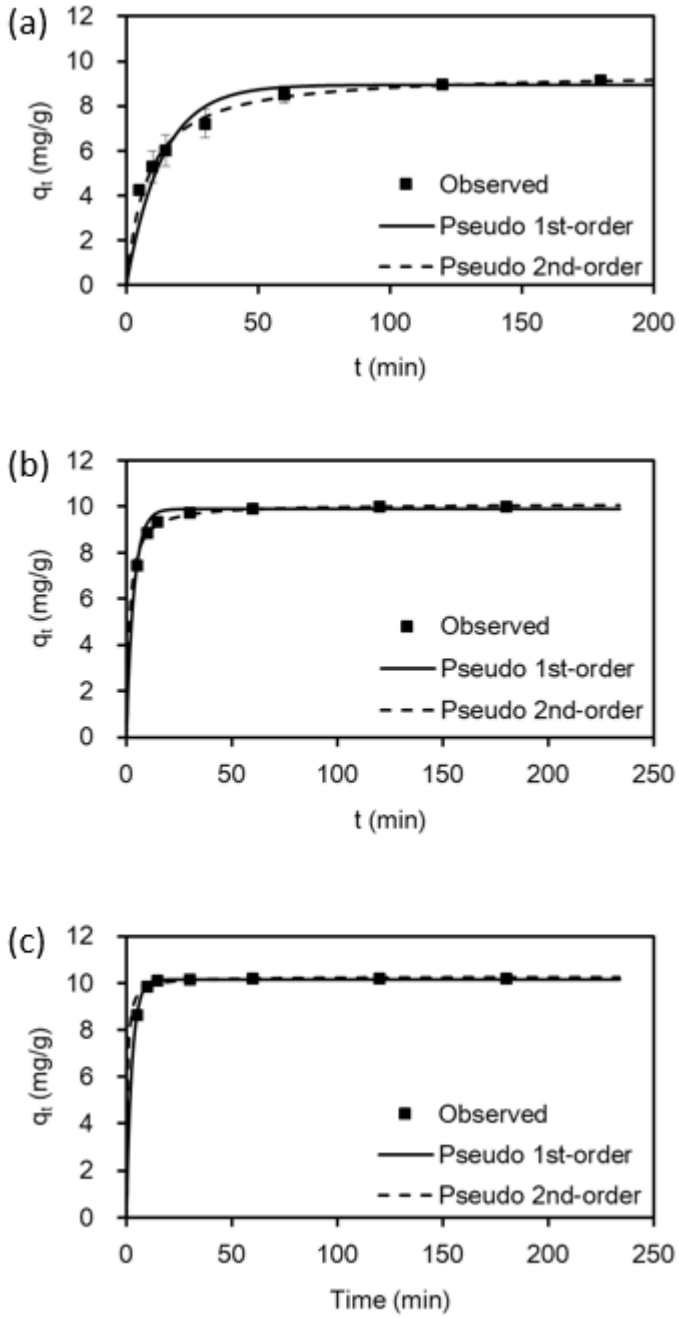

Fig. 15. Kinetic data and model fits for Cr(VI) removal by anion exchange fibers: (a) KC31; (b) SA; (c) SA2

Table 12. Model parameters of pseudo first and pseudo second kinetic model obtained from model fitting to Cr(VI) kinetic data

	Pseudo first model					Pseudo second model				
	k_1 (1/min)	q_e (mg/g)	R^2	χ^2	SAE	k_2 (g/mg/min)	q_e (mg/g)	R^2	χ^2	SAE
KC31	0.074	8.95	0.950	0.960	3.36	0.013	9.53	0.983	0.118	1.25
SA	0.279	9.91	0.942	0.042	1.19	0.068	10.1	0.983	0.024	0.670
SA2	0.379	10.2	0.993	0.001	0.22	0.223	10.3	0.889	0.071	1.05

4.4. Regeneration of ion exchange fibers

The results of regeneration experiments using anion exchange fibers were presented in Fig. 16. During the five adsorption-desorption cycles, the removal capacity of anion exchange fibers did not dropped significantly. In case of KC31, as first regeneration process was carried out, the removal capacity of fibers was slightly increased. It could be because the protonated amine groups during the Cr(VI) adsorption didn't lose their protons at the desorption process. However, in case of SA2, the removal capacity of fibers was slightly decreased as it reused.

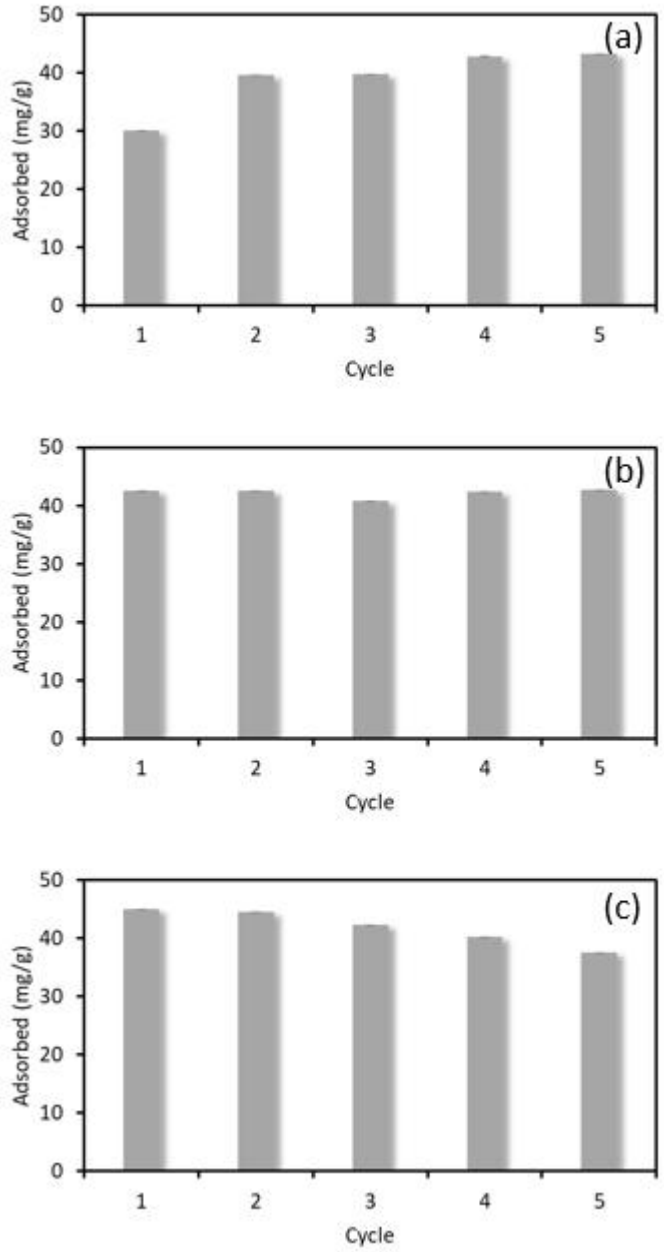

Fig. 16. Regeneration and reuse of anion exchange fibers over five Cr(VI) adsorption-desorption cycles: (a) KC31; (b) SA; (c) SA2

5. Cr(VI) removal from chromium-plating rinse water

The Cr(VI) breakthrough curves obtained from column experiments with chromium-plating rinse water are presented in Figure 17. In Exp. 1 (flow rate = 0.5 mL/min), Cr(VI) concentrations were below 1.0 mg/L until 50 h, increased gradually to 164 mg/L after 73 h, and rose sharply thereafter to 1178 mg/L after 640 hours. In Exp. 2 (flow rate = 1.0 mL/min), Cr(VI) concentrations were below 1.0 mg/L until 20 h and then increased rapidly to 1178 mg/L at 57 hours. As the flow rate increased, a steeper breakthrough curve was observed because the driving forces were enhanced, and the length of the adsorption zone was reduced (Kim et al., 2009).

The Cr(VI) removal capacities for KC31 in Exp. 1 and Exp. 2 were 214.8 and 171.5 mg/g, respectively. As the flow rate increased, the Cr(VI) removal capacity decreased because the contact time between Cr(VI) ions and KC31 decreased; the EBCT decreased from 98.2 to 49.1 min with an increase in the flow rate from 0.5 to 1.0 mL/min. Model parameters for the fixed-bed kinetic sorption models are presented in Table 13. The breakthrough curves were well described by

the models. In the case of the Bohart–Adams model, the rate constant (k_{BA}) increased with the increasing flow rate from 0.5 (Exp. 1) to 1.0 mL/min (Exp. 2), whereas the removal capacity (N_0) decreased with the increasing flow rate. For the Clark model, the model constant (A) decreased, but the rate constant (r) increased with the increasing flow rate. For the modified dose-response model, both the model constant (a) and the removal capacity (q_0) decreased with the increasing flow rate.

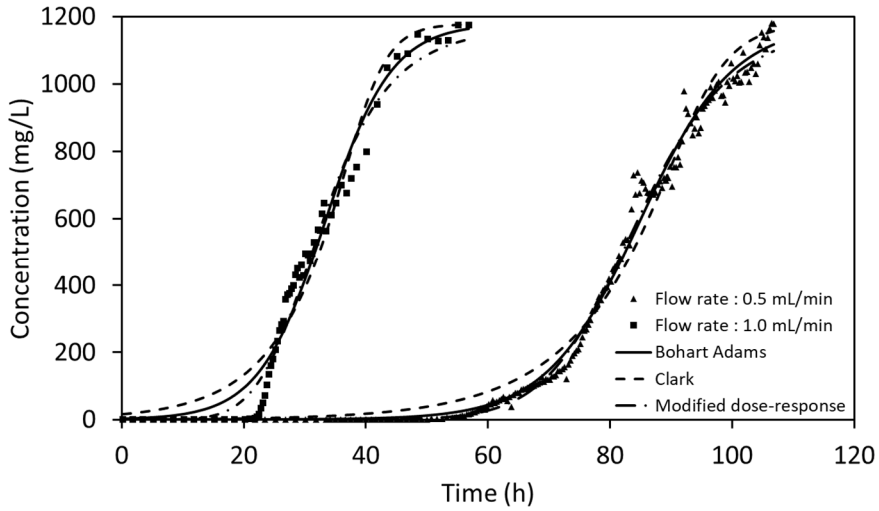

Fig. 17. Breakthrough curves and model fits of fix-bed kinetic sorption models for Cr(VI) removal in chromium-plating rinse water by KC31 fibers under flow-through column conditions

Table. 13. Model parameters for fixed-bed kinetic sorption models obtained from the breakthrough curves for Cr(VI) removal column experiment

	Bohart-Adams			Clark			Modified dose-response		
	K_{BA} (L/h/g)	N_0 (g/L)	R^2	A	r (1/h)	R^2	a	q_0 (mg/g)	R^2
Exp. 1	0.11	76.3	0.99	3.3×10^9	0.23	0.98	11.0	214.3	0.99
Exp. 2	0.16	59.9	0.97	5.6×10^5	0.33	0.96	5.9	166.9	0.98

5. Conclusions

Anion exchange fibers were tested for removing arsenate and chromate from synthetic water and wastewater. KC31 has free amine form of functional groups. SA has fully protonated amine as functional groups. SA2 has half of protonated amine and half of free amine as its functional groups. Experiments for pH showed that the fibers reacts differently at pH changes in the removal of toxic anions. The maximum removal capacity for As(V) and Cr(VI) of three fibers from Langmuir models were 47.16, 250.2 mg/g (KC31), 47.19, 162.5 mg/g (SA), and 38.05, 161.0 mg/g (SA2), respectively. In the regeneration tests, the fibers could be successfully regenerated over five adsorption-desorption cycles using NaCl solution. Column experiments represented that KC31 could remove As(V) and Cr(VI) properly in spite of the presence of other anions (sulfate, phosphate, nitrate etc.). The results from this study represented that the anion exchange fibers are applicable to remove arsenate and chromate in various kinds of water.

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국문 초록

본 논문에서는 모드아크릴 음이온교환섬유에 대한 다양한 특성 분석을 실시하고 이온교환섬유를 이용하여 합성폐수 내의 5가 비소와 6가 크롬을 제거하였다. Kanecaron사에서 개발한 KC31, SA, SA2의 세 음이온교환섬유의 물리화학적 특성과 그러한 특성들이 섬유의 5가 비소와 6가 크롬의 제거에 미치는 영향에 대하여 꼼꼼하게 살펴보았다.

FE-SEM 분석을 통하여 세 이온교환섬유가 약 20 마이크로미터 직경의 원기둥형 섬유라는 것을 확인하였다. EDS 분석 결과를 통하여 이온교환섬유의 구성 원소가 탄소 (C), 질소 (N), 산소 (O), 그리고 염소 (Cl)임을 알 수 있었으며, 이 원소들은 모드아크릴 섬유의 구성요소인 아크릴로니트릴 (acrylonitrile)과 비닐 클로라이드 (vinyl chloride)에서 기인한 것으로 보인다. 이온교환용량 실험을 통하여 KC31은 양자화되지 않은 4.70 mmol/g의 아민기를 기능기로 가지고 있음을 알 수 있었고, SA는 1.15 mmol/g의 양자화된 아민기를 가지고 있었으며, SA2는 총 2.65 mmol/g의 기능기 중 1.34 mmol/g가 양자화된 아민기였다.

pH 실험 결과, KC31은 pH 4에서 5가 비소에 대한 흡착능이 가장 높았고 (9.480 mg/g), 6가 크롬에 대한 흡착능은 pH 2에서 가장 높았다 (47.89 mg/g). SA의 경우, 5가 비소에 대한 흡착능은 pH 10에서 가장 높았으며 (9.753 mg/g), 6가 크롬에 대한 흡착능은 pH 4에서 가장 높았다 (47.16 mg/g). SA2의 5가

비소에 대한 흡착능은 pH 10에서 가장 높았으며 (8.419 mg/g), pH 6에서 6가 크롬에 대한 가장 높은 흡착능을 가졌다 (48.99 mg/g). Langmuir isotherm model에서 최대 흡착능을 도출하였을 때, KC31의 5가 비소에 대한 최대 흡착능은 47.16 mg/g, 6가 크롬에 대한 최대 흡착능은 250.2 mg/g이었으며, SA의 5가 비소에 대한 최대 흡착능은 47.19 mg/g, 6가 크롬에 대한 최대 흡착능은 162.5 mg/g이었고, SA2의 경우 각각 38.05 mg/g, 161.0 mg/g이었다. Kinetic 실험 결과, 세 이온교환섬유는 5가 비소와 6가 크롬과 반응하여 모두 1 시간 내에 평형에 도달함을 알 수 있었다. NaCl 용액을 이용하여 5가 비소와 6가 크롬을 흡착한 세 이온교환섬유를 모두 효과적으로 재생하였으며, 재생 후의 흡착능은 크게 변하지 않았다.

산성의 광산폐액과 크롬 도금 수세수를 처리하기에 KC31이 가장 적합한 이온교환섬유로 선정되었다. KC31은 칼럼 실험 조건에서 폐액 내에 포함된 다량의 5가 비소와 6가 크롬을 제거하였다.

본 연구 결과를 통해, 모드아크릴 음이온교환섬유를 활용하여 산업폐수 내 5가 비소와 6가 크롬을 효과적으로 제거할 수 있음을 확인하였다.

주요어: 모드아크릴 섬유, 이온교환섬유, 5가 비소, 6가 크롬, 중금속, 폐수 처리

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